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Persistence of chlorpyrifos in greenhouse air

Persistência do inseticida clorpirifós no ar em casa de vegetação

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ABSTRACT: Organophosphate pesticides are among those with the highest acute toxicity and are available on the market and used in several regions of Brazil. The concentration and residence time of the organophosphate pesticide, chlorpyrifos, in the air after application in a greenhouse were investigated. For more than 24 h, the chlorpyrifos remained in the greenhouse air at concentrations three times above the occupational exposure limit and was still detectable four days later.

KEYWORDS: organophosphate insecticides, occupational exposure, re-entry period.

RESUMO: Os inseticidas organofosforados estão entre os agrotóxicos de maior toxicidade aguda disponíveis no mercado e são usados em várias regiões do Brasil. Avaliaram-se a concentração e o tempo de permanência do inseticida organofosforado clorpirifós no ar, após aplicação em uma casa de vegetação. O clorpirifós permaneceu no ar da casa de vegetação em concentração três vezes acima do limite de exposição ocupacional por mais de 24 horas, e ainda foi detectado após quatro dias.

PALAVRAS-CHAVE: inseticidas organofosforados, exposição ocupacional, período de reentrada.

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Pesticides are related to acute poisoning, chronic diseases, and reproductive problems. It is estimated that, among workers in developing countries, pesticides annually cause 70 thousand fatal acute and chronic poisonings and at least 7 million nonfatal acute and chronic diseases (Faria et al., 2007). Brazil has been the largest consumer of pesticides in the world since 2008 and is responsible for 86% of their consumption in Latin America (Santana et al., 2013). Data from the Federal Ministry of Health show that from 2008 to 2013, an annual average of 1,560 confirmed cases of poisoning, exposure, and adverse reaction to pesticides occurred (Brasil, 2014).

Organophosphates are among the most acutely toxic pesticides available on the market, and the registrations of different active ingredients for such have been cancelled in several countries, including Brazil (Pasiani et al., 2012). Organophosphates are acetylcholinesterase inhibitors, and exposure to these pesticides causes adverse health effects such as nausea, bronchoconstriction, sialorrhea, hypertension, and tremors, in addition to affecting the central nervous system (Pasiani et al., 2012). Of the total deaths caused by pesticide poisoning in the State of São Paulo, from 1998 to 2005, 20.9% corresponded to organophosphate products (São Paulo, 2014).

Nevertheless, because of their efficiency, relatively low cost, and absence of bioaccumulation in the ecosystem, organophosphates are still widely used, despite the availability of other classes of pesticides (Costa, 2006). Organophosphates are used extensively in agriculture in different regions of Brazil (Faria et al., 2009; Stroparo; Braguini, 2011; Pasiani et al., 2012; Ribeiro et al., 2012), probably due to the large number of brands still available on the market and factors such as low cost and traditional use by farmers (Lima et al., 2011).

It is estimated that, in Brazil, production of flowers, fruits, and vegetables in protected environments, such as greenhouses, occupies approximately 26,000 hectares, half of which are located in the State of São Paulo (Figueiredo, 2011). In protected cultivation, the use of synthetic chemical compounds is the most common control measure, and is often believed to be the most effective for pest control (Vida et al., 2004). However, information such as efficiency, dosage, application intervals, persistence, and confidence interval is available only for crops in conventional cultivation and are scarce for protected cultivation (Vida et al., 2004). Occupational exposure to pesticides may be prolonged and intensified by environmentally specific conditions in protected cultivation such as high temperature, high humidity, and poor ventilation (Jurewicz et al., 2009; Ribeiro et al., 2012). Furthermore, as protected cultivation requires intensive care, workers are exposed more frequently to pesticides, especially those dispersed in confined areas (Siebers; Mattusch, 1996). Despite this fact, there are few studies in this regard and, in Brazil, there are no specific guidelines or regulations for greenhouse activities (Ribeiro et al., 2012).

The health risk to a worker who performs activities inside closed places where pesticides are used, such as greenhouses and other protected environments, may be estimated by measuring the concentration of these products in the environment. Determining an appropriate re-entry period ensures that a worker can re-enter the treated area safely without personal protective equipment (PPE) (Choi et al., 2013). However, specific re-entry periods for production in protected cultivation have not been established (USEPA, 2006).

Despite the possible health risks related to re-entry into greenhouses after the application of pesticides, few studies have been carried out regarding the persistence of pesticides in a protected cultivation environment (Hatzilazarou et al., 2004). In this study, we evaluate the concentration and permanence time of the organophosphate pesticide, chlorpyrifos in the air after its application inside a greenhouse, to estimate the risk of exposure of a worker in this environment.

The study was conducted at the Biologic Institute (São Paulo, Brazil) during the summer time, in a glass experimental greenhouse with an area of 48 m^2 (10 × 4.8 m) and a volume of 168 m^3. During the study, the greenhouse remained unventilated and fully closed. Inside the greenhouse, the temperature and relative humidity ranged from 30.0°C to 30.8°C and from 61.6 to 70.1%, respectively.

The pesticide used in the study was a commercial product, available on the market as an emulsifiable concentrate formulation, containing chlorpyrifos, at the concentration of 480 g/L, as the active ingredient. Chlorpyrifos is an organophosphate insecticide, formicide, and acaricide, with authorized agricultural use for foliar and soil applications for different crop cultures (ANVISA, 2014). It has 1.87×10^{-5} mmHg vapor pressure at 20°C (USEPA, 2006), is moderately toxic by inhalation (USEPA, 2006), and is one of the 10 most marketed active ingredients with insecticidal action in Brazil (IBAMA, 2009).

The product was applied at a dose of 100 mL in 10 L of water, as recommended by the manufacturer, with a manual compression spray, at 1.50 m above the floor of the greenhouse. A spray nozzle with a flat fan tip produced droplets with a volume median diameter calculated to be between 200 µm and 400 µm. Immediately after application and at 24, 48, 72, and 96 h post-application, air samples were collected at a height of 1.80 m from the greenhouse floor using a Supelco polyurethane foam (PUF) ORBO™ 1000 attached to a vacuum pump with a flow of 6 L/min operating for 5 min. This setup allowed for the sampling of the pesticide in a volume of 30 L of air. The pesticide was extracted from the PUF cartridge with 60 mL of ethyl acetate using a 40-kHz ultrasound bath for 6 min. The extract was concentrated to dryness and then dissolved in 1.5 mL of methanol. This solution was filtered through a 45-µm syringe filter and then analyzed by high-performance liquid chromatography (HPLC). The chromatographic analysis was performed using an HPLC system

(Dionex UltiMate® 3000), with a C18 column, mobile phase of methanol:water of 82:18 (v/v), 1 mL/min flow, temperature of 35°C, UV detector wavelength of 275 nm, and linear calibration curve calculated from concentrations of 0.4, 0.8, 1.6, 3.2, and 6.4 µg/mL.

The chlorpyrifos applied inside the greenhouse remained in the air throughout the study period. The highest concentrations were found immediately after the application and after 24 h. Over time, the product dissipated; however, even after 96 h, it was still detected in the ambient air (Fig. 1). Hatzilazarou et al. (2005) reported the highest concentrations of chlorpyrifos 2 h after the application (7.1 µg/m³) and a decrease in concentration in the following days, reaching 0.16 µg/m³ after 6 days. In another study, the concentration of chlorpyrifos in the air decreased by 50% 3 h after the application, and after 2 h of ventilation, the pesticide was not detected (Guardino et al., 1998). The variation in the concentration of chlorpyrifos among these studies may be explained by the difference in climatic conditions and greenhouse characteristics. In this study, the characteristically high temperatures of summer, relatively small size of the greenhouse, and lack of ventilation promoted the volatilization of chlorpyrifos and hampered its dissipation. All these factors increase the risk of exposure to workers when they return to the environment after product application.

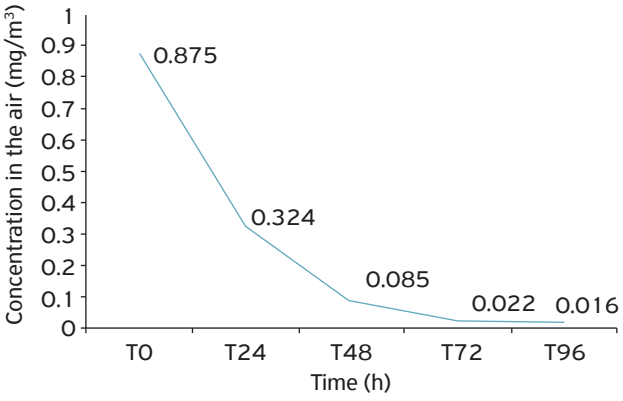

Figure 1. Chlorpyrifos pesticide concentration in the greenhouse air.

According to Brouwer et al. (1992), risk to a worker's health exists when the product concentration exceeds the occupational exposure limit. The occupational exposure limit, called a threshold limit value (TLV), set by the American Conference of Governmental Industrial Hygienists for chlorpyrifos in the form of vapor or inhalable aerosols, is 0.1 mg/m³ (Christensen et al., 2009). In this study, the concentration of chlorpyrifos in the air, 24 h after the application, was 0.324 mg/m³, which exceeds the TLV over three-fold. After 48 h, this value decreased to 0.085 mg/m³, which is below the occupational exposure limit. Therefore, the organophosphate pesticide chlorpyrifos did not dissipate, and remained in the greenhouse air at a concentration three times higher than the established occupational exposure limit for more than 24 h.

In the specific conditions of this study, the safe return of a worker without PPE to the treated environment should only occur 48 h after spraying of the product. The re-entry interval in open areas established by the United States Environmental Protection Agency (USEPA) to environments treated with chlorpyrifos ranges from 24 h to 10 days, depending on the environment. However, there is no specific re-entry interval for protected cultivation environments (USEPA, 2006).

Considering the toxicity of chlorpyrifos, the absence of a specific re-entry interval for greenhouses, and the fact that this pesticide is widely used in Brazil, it is important to adopt preventive measures, such as ventilation of the environment, use of PPE, and a proper reentry interval, to ensure a worker's safety after the application of this pesticide in a greenhouse.

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